

Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

By CRAIG L. SPRINKLE

REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1403-I



for carbonate mineral dissolution or precipitation, depending on the ratio of freshwater to seawater in the mixture. In areas where flow is sluggish, remnant gypsum or seawater may increase concentrations of major chemical elements above 1,000 mg/L. The reaction models also indicate that fluxes of carbon occur throughout the flow system, even in areas where the Upper Floridan aquifer is thickly confined. These nonzero carbon fluxes complicate interpretation of ^{14}C data and computation of flow velocities from radiometric dating of water "age."

SUMMARY

The Floridan aquifer system occurs in parts of four southeastern States and is one of the most productive aquifer systems in the world. More than 3 billion gallons of water are pumped from the aquifer system daily, yet there are tremendous untapped reserves of freshwater. Near some urban centers, intensive development of the ground-water resource has led to declining water levels and localized water-quality degradation.

The region underlain by the Floridan aquifer system has a climatic range from temperate to subtropical; annual precipitation (mostly rainfall) generally ranges from 40 to 65 in. The chemistry of major ions in precipitation is dominated by salts in sea spray, except for Na^+ and SO_4^{2-} ; sources of the additional Na^+ and SO_4^{2-} are speculative at this time.

The Floridan aquifer system is a vertically continuous sequence of Tertiary carbonate rocks of generally high permeability. Limestones and dolomites are the principal rock types in the aquifer system, although in southwestern and northeastern Georgia and in adjacent South Carolina, the limestones grade into limy sands and clays. The Floridan is composed primarily of calcite and dolomite. Minor minerals include gypsum, apatite, glauconite, quartz (or chert), clay minerals (kaolinite and montmorillonite), and trace amounts of metallic oxides and sulfides.

The aquifer system generally consists of an Upper and Lower Floridan aquifer separated by a less permeable confining unit having highly variable hydraulic properties. The Upper Floridan aquifer is present throughout the study area; the Lower Floridan aquifer is not present in most of northern Florida and Georgia. Recharge occurs primarily in outcrop areas of Alabama, Georgia, and north-central Florida. Most discharge is to rivers and springs; only about 5 percent of the predevelopment discharge was directly into the sea. The quantity of ground-water flow in the system is affected by the extent of confinement. Where the system is unconfined, recharge is rapid and plentiful, ground-water circulation and discharge rates are high, and secondary permeability is developed by mineral dissolution. Where confining

units are thick, the carbonate chemistry of the ground water evolves in a closed system and development of secondary permeability is slow. A secondary chemical effect of confinement is reduction in the rate of flushing of (residual) salty water from the aquifer system.

After review of about 52,000 chemical analyses of water from more than 7,000 wells, a subset of 601 analyses (representing 601 wells) was chosen to characterize the chemistry of major ions in the Upper Floridan. Because fewer than 100 wells penetrating the Lower Floridan aquifer were available during the study, the regional description of the Lower Floridan is limited to maps that show estimated Cl^- and dissolved-solids concentrations. Description of chemical patterns within the Upper Floridan aquifer required interpretation of chemical data from water samples collected at different depths, because of mixing that occurs within the open-bore wells commonly drilled in the aquifer. Mixing affects water chemistry by (1) modifying temperatures, (2) changing environmental isotope ratios, (3) changing ionic strength, (4) changing net partial pressures of dissolved gases, and (5) altering solution pH and Eh.

Regional hydrogeochemistry is depicted in maps that show the distribution and concentration of major cations and anions, selected minor elements, and nutrients. Calcium is the major cation in fresh ground water; concentrations generally range from 5 to 570 mg/L. The concentration of Ca^{2+} is controlled primarily by calcite saturation, although gypsum solubility may locally be the geochemical control. Gypsum dissolution can cause dedolomitization of the aquifer, but sulfate and magnesium concentrations and lack of significant sulfate reduction indicate that dedolomitization dissolves less than 0.5 mmol of dolomite per liter of water over much of the Floridan's area of occurrence. Concentrations of Mg^{2+} in the Upper Floridan aquifer generally range from 1 to 1,000 mg/L; the highest Mg^{2+} concentrations occur where the Upper Floridan contains seawater. Where the aquifer contains freshwater, Mg^{2+} concentrations generally increase in downgradient directions because of dedolomitization of the aquifer. Data are insufficient to prove that formation of dolomite limits Mg^{2+} concentrations in the Upper Floridan. The lowest concentrations of Na^+ and K^+ are nearly equal to the concentrations in rainfall—about 1 mg/L of Na^+ and 0.2 mg/L of K^+ . In coastal areas, Na^+ concentrations exceed 500 mg/L and K^+ concentrations exceed 20 mg/L. Cation exchange is indicated in parts of Georgia and in the Florida Panhandle where Na^+/Cl^- and K^+/Cl^- ratios are high. Moderately high Na^+/Cl^- and K^+/Cl^- ratios in the Upper Floridan aquifer in southwestern Georgia may be due to inflow from the underlying or adjacent sand aquifers, but may also result from Na^+ and K^+ added to ground water by leaching of fertilizers on the land surface.

The principal anions in the ground water are HCO_3^- , Cl^- , and SO_4^{2-} . Carbonate buffering in the Upper Floridan aquifer maintains the pH of ground water within the range 7.0 to 8.5. Bicarbonate is the principal anion in freshwater areas, and concentrations of HCO_3^- range from 122 to 244 mg/L; this reflects the control that calcite solubility exerts over HCO_3^- concentrations. The high HCO_3^- concentrations in extreme western Florida apparently result from cation-exchange-driven carbonate disequilibrium. Concentrations of Cl^- are nearly zero in recharge areas; the highest Cl^- concentrations are found where seawater is present in the Upper Floridan aquifer. Regionally, shallow wells completed in the Upper Floridan yield water having Cl^- concentrations of less than 250 mg/L and may be an adequate source of supply for domestic or industrial purposes. The high Cl^- concentrations along the St. Johns River and the eastern coast of Florida and in southern Florida may be due to incomplete flushing of Pleistocene seawater. High Cl^- concentrations in parts of the aquifer near coastal cities in Georgia and Florida are related to pumpage. Concentrations of SO_4^{2-} range from about zero in recharge areas to more than 3,500 mg/L in deep gypsiferous units. Bisulfide (HS^-) occurs throughout the aquifer system in low concentrations (<1 mg/L) as a result of sulfate reduction, but the amount of HS^- measured in water samples may indicate only a fraction of the total sulfide actually formed.

The major geochemical processes that occur in the Upper Floridan aquifer are

1. Dissolution of aquifer minerals toward equilibrium;
2. Mixing of ground water with seawater, recharge, or leakage;
3. Sulfate reduction; and
4. Cation exchange between water and rock minerals.

In recharge areas, calcite dissolution produces ground water that is calcium-bicarbonate dominated, and dissolved-solids concentrations are generally less than 250 mg/L. Downgradient, dissolution of dolomite leads to a calcium-magnesium-bicarbonate hydrochemical facies. Where gypsum is abundant, sulfate becomes the predominant anion. In coastal areas, seawater increases the dissolved-solids concentrations and hydrochemical facies change to sodium chloride. Leakage from underlying or adjacent sand aquifers in south-central Georgia enters the Upper Floridan and lowers dissolved-solids concentrations but does not change the hydrochemical facies. In the western panhandle of Florida, cation exchange leads to development of a sodium-bicarbonate facies.

The same processes that control the occurrence and distribution of major constituents also control the occurrence of many minor constituents. Concentrations of F^- range from about zero near the outcrop to about 4 mg/L in western Florida; over most of the study area, the F^-

concentration is less than 1.0 mg/L, well within the maximum contaminant level for drinking water. The principal source of F^- in freshwater is recharge; once F^- enters the system, it appears to be chemically conservative. Concentrations of dissolved silica range from about 1 to about 80 mg/L; highest concentrations occur in Georgia and South Carolina. Silica concentrations appear to be controlled by the solubility of quartz or chalcedony. Low concentrations of P (phosphorus species) occur throughout the Upper Floridan aquifer; 75 percent of water samples from the aquifer contained less than 0.1 mg/L of total P. No mineral sources of N (nitrogen) species have been detected within the aquifer system, yet moderate concentrations have been detected in water samples. Statistical tests indicate that the aquifer system has a uniform total N concentration, although man's activities may be affecting concentrations of N species in unconfined recharge areas. Areal differences in N-species concentrations indicate that nitrate reduction may be important in controlling N concentrations. Denitrification may significantly reduce N concentrations in unconfined areas of the aquifer system, but further studies are needed to confirm this hypothesis.

Data on the occurrence of trace metals, stable isotopes and radioisotopes, and organic contaminants in the Floridan aquifer system are very limited. Almost all water samples that have been analyzed for trace metals are within drinking water standards, although most samples have been analyzed for only iron and manganese. High trace metal concentrations are uncommon in the Upper Floridan aquifer and are generally related to a nearby contaminant source or to faulty well construction. Selected data on stable isotopes of O, H, and C were compiled on a regional basis for the first time. Available ^{14}C data were also compiled, but use of the ^{14}C data to compute ground-water flow velocities is hindered by the lack of stable isotope data on reacting phases. Other natural radioisotopes are present in such low concentrations that their hydrologic significance is difficult to determine. A product of uranium decay, Ra-226, has been reported in concentrations that exceed drinking water standards (5 pCi/L) in wells in southwestern Florida, but the exact sources and processes that control Ra-226 concentrations have not been determined. Analyses of organic compounds determined by the Geological Survey date back to about 1960, but many manmade organic compounds were first analyzed as recently as 1982. The majority of organic compounds tested were below the threshold of detection; however, detection of manmade organic compounds in a few samples indicates that the flow system is susceptible to contamination in some areas.

Plausible reaction models of downgradient changes in chemical composition indicate that the geochemistry of

the Upper Floridan aquifer is dominated by the dynamic nature of the flow system. In unconfined areas, large volumes of dilute water recharge the system, dissolve minerals in the aquifer matrix, and enhance permeability. In coastal areas, mixing of freshwater with seawater creates the potential for calcite and dolomite dissolution or precipitation, depending on the ratio of freshwater to seawater in the mixture. In areas where flow is more sluggish, concentrations of major elements are increased by dissolution of gypsum or mixing with residual saline water. Ion exchange and sulfate reduction are plausible reaction models in parts of the system. Reaction models indicate that a nonzero carbon flux occurs in almost all parts of the system; this complicates the use of ^{14}C measurements to determine ground-water-flow velocities.

SELECTED REFERENCES

- Altschuler, Z.S., Clarke, R.S., Jr., and Young, E.J., 1958, Geochemistry of uranium in apatite and phosphorite: U.S. Geological Survey Professional Paper 314-D, p. 45-90.
- Back, William, 1960, Origin of hydrochemical facies of ground water in the Atlantic Coastal Plain; International Geological Congress, Geochemical Cycles: International Geological Congress, 21st, Copenhagen, Denmark, 1960, Proceedings, pt. 1, p. 87-95.
- , 1963, Preliminary results of a study of calcium carbonate saturation of ground water in central Florida: International Association of Scientific Hydrology, VIII Annue, no. 3, p. 43-51.
- , 1966, Hydrochemical facies and ground-water flow patterns in northern part of Atlantic Coastal Plain: U.S. Geological Survey Professional Paper 498-A, 42 p.
- Back, William, and Hanshaw, B.B., 1970, Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan: *Journal of Hydrology*, v. 10, p. 330-368.
- Back, William, Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., and Rubin, Meyer, 1983, Process and rate of dedolomitization: Mass transfer and ^{14}C dating in a regional carbonate aquifer: *Geological Society of America Bulletin*, v. 94, p. 1415-1429.
- Back, William, Hanshaw, B.B., Pyle, T.E., Plummer, L.N., and Weidie, A.E., 1979, Geochemical significance of ground water discharge and carbonate solution to the formation of Caleta Xel Ha, Quintana Roo, Mexico: *Water Resources Research*, v. 15, no. 6, p. 1521-1535.
- Back, William, Hanshaw, B.B., and Rubin, Meyer, 1970, Carbon-14 ages related to occurrence of saltwater: *Journal of Hydraulics Division of American Society of Civil Engineers*, v. 96, no. HY11, p. 2325-2336.
- Badiozamani, Khosrow, 1974, The Dorag dolomitization model—Application to the Middle Ordovician of Wisconsin: *Journal of Sedimentary Petrology*, v. 43, no. 4, p. 965-984.
- Baes, C.F., Jr., and Mesmer, R.E., 1976, The hydrolysis of cations: New York, John Wiley, 489 p.
- Ball, J.W., Nordstrom, D.K., and Jenne, E.A., 1978, Additional and revised thermochemical data and computer code for WATEQ2—A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters: U.S. Geological Survey Water-Resources Investigation 78-116, 114 p.
- Barker, R.A., 1986, Preliminary results of a steady-state ground-water flow model of the Southeastern Coastal Plain aquifer system, in *Southern Regional Ground-Water Conference*, San Antonio, Tex., September 18-19, 1985, Proceedings: Association of Ground-Water Scientists and Engineers and National Water Well Association, p. 315-338.
- Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.
- Barnes, R.B., 1975, The determination of specific forms of aluminum in natural water: *Chemical Geology*, v. 15, no. 3, p. 177-191.
- Barracough, J.T., and Marsh, O.T., 1962, Aquifers and quality of ground water along the Gulf Coast of western Florida: Florida Geological Survey Report Investigation 29, 28 p.
- Baturin, G.N., Kochenov, A.V., and Petelin, V.P., 1970, Phosphorite formation on the shelf of southwest Africa: *Litologiya i Poleznye Iskopaemye* [Lithology and Mineral Resources—Engl. trans.], v. 3, p. 266-276.
- Behrens, E.W., and Land, L.S., 1972, Subtidal Holocene dolomite, Baffin Bay, Texas: *Journal of Sedimentary Petrology*, v. 42, p. 155-161.
- Bigeleisen, J., Perlman, M., and Prosser, H., 1952, Conversion of hydrogenic materials to hydrogen for isotopic analysis: *Analytical Chemistry*, v. 24, p. 1356-1357.
- Bogli, Alfred, 1964, Mischungskorrosion—ein Beitrag zum Verkarsungsproblem: *Bonn, Erdkunde*, v. 18, p. 83-92.
- Briel, L.I., 1976, An investigation of the U234/U238 disequilibrium in the natural waters of the Sante Fe River basin of north-central Florida: Unpub. Ph.D. dissertation, Florida State University (Tallahassee), 241 p.
- Brown, D.P., 1980, Geologic and hydrologic data from a test-monitor well at Fernandina Beach, Florida: U.S. Geological Survey Open-File Report 80-347, 39 p.
- , 1984, Impact of development on availability and quality of ground water in eastern Nassau County, Florida, and southeastern Camden County, Georgia: U.S. Geological Survey Water-Resources Investigations 83-4190, 133 p.
- Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 160 p. (superseded)
- Brown, W.E., 1960, Behavior of slightly soluble calcium phosphates as revealed by phase-equilibrium calculations: *Soil Science*, v. 90, p. 51-57.
- Bush, P.W., 1982, Predevelopment flow in the Tertiary limestone aquifer, southeastern United States: A regional analysis from digital modeling: U.S. Geological Survey Water-Resources Investigations 82-905, 41 p.
- Bush, P.W., and Johnston, R.H., 1988, Ground-water hydraulics, regional flow, and ground-water development of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama: U.S. Geological Survey Professional Paper 1403-C.
- Chapelle, F.H., 1983, Groundwater geochemistry and calcite cementation of the Aquia aquifer in southern Maryland: *Water Resources Research*, v. 19, no. 2, p. 545-558.
- Chapelle, F.H., and Knobel, L.L., 1983, Aqueous geochemistry and the exchangeable cation composition of glauconite in the Aquia aquifer, Maryland: *Ground Water*, v. 21, no. 3, p. 343-352.
- Chien, S.H., and Black, C.A., 1976, Free energy of formation of carbonate apatites in some phosphate rocks: *Soil Science Society of America Journal*, v. 40, p. 234-239.
- Claassen, H.C., 1982, Guidelines and techniques to obtain valid ground-water quality samples: U.S. Geological Survey Open-File Report 82-1024, 54 p.